

PATENT SPECIFICATION

(11) 1289 156

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NO DRAWINGS

- (21) Application No. 54549/69 (22) Filed 6 Nov. 1969
- (31) Convention Application No. 81554 (32) Filed 6 Nov. 1968
- (31) Convention Application No. 10330 (32) Filed 12 Feb. 1969 in
- (33) Japan (JA)
- (45) Complete Specification published 13 Sept. 1972
- (51) International Classification C08F 47/08 C01B 31/08
- (52) Index at acceptance

C3C 1B1 1C
B1L 5B2
C1A K4
C3P 1A 1C15 1C4B 1C8B 1C8C 1D1A 1D1B 1D5 1F2



(54) POROUS ADSORBENT MATERIAL AND PRODUCING THE SAME

5 (71) We, KABUSHIKI KAISHA KURARAY, formerly Kurashiki Rayon Kabushiki Kaisha, of 1621, Sakazu, Kurashiki City, Japan, a Company organised according to the laws of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to porous adsorbent materials consisting essentially of a polyvinyl acetal resin and a particulate adsorbent or a mixture of adsorbents, optionally containing an inorganic filler. The invention also relates to a process for manufacturing such a material.

15 Adsorbents, such as active carbon, have generally been used in the form of a powder, granules or tablets and it has been impossible to shape them into desired shapes such as sheets, string, pipes or rods by extruding or moulding using techniques applicable to plastics materials. Therefore, these adsorbents must be used packaged in perforated cases to avoid their loss. However, in practice this proves inconvenient and also renders more difficult the desorption of the adsorbents with steam to regenerate their adsorptive ability.

20 The adsorbent materials of the present invention may be manufactured in the form of a flexible sheet, which can be rolled up, or in the form of granular moulding materials which can give any desired shape by compression moulding. Moreover, the adsorbent materials have a continuous porous structure, which affords a wide field of application which was not available with conventional adsorbent materials.

25 Thus, the present invention consists in an adsorbent material having a continuous porous structure, which comprises a uniform dispersion of particulate active carbon in a poly-

vinyl acetal resin, the amount of active carbon being from 0.5 to 20 parts by weight per part by weight of said resin. The materials may be prepared using the polyvinyl acetal resin as a binder for the active carbon adsorbent and utilising a wet-coagulation technique. Specifically, the adsorbent is introduced into a solution of the resin in a water-miscible solvent in an amount of from 0.5 to 20 parts by weight per part by weight of the resin and the resulting mixture is mixed e.g. kneaded to give a fluid mixture, which is then put into the desired shape if required and contacted with an aqueous coagulation liquid to effect wet-coagulation and thus obtain the adsorbent material of the invention.

30 The structure of the material of the present invention is referred to herein as "continuous porous": by this we mean that the structure comprises a plurality of interconnected pores defining continuous capillaries, so that the material is rendered permeable to fluid and so that the particles of active carbon adsorbent are available to the fluid.

35 Examples of suitable polyvinyl acetal resins include water-insoluble resins such as polyvinyl formal resin, polyvinyl acetal resin itself and polyvinyl butyral resin. These resins should preferably have a degree of acetalization of at least 50 mol %, and the most desirable resin is polyvinyl formal resin. We have found that, in order to produce suitable adsorbent materials, it is necessary to use these resins and that other resins, such as polystyrene, polyvinyl chloride, polyethylene and polyurethanes, are unsuitable.

40 The polyvinyl acetal resin of the present invention is prepared by reacting a polyvinyl alcohol with an aldehyde, such as formaldehyde, acetaldehyde or butyraldehyde. The percentage of the total number of hydroxyl groups of the polyvinyl alcohol which have been condensed with the aldehyde to form

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- acetal bonds (e.g. formal, acetal itself or butyral bonds) is referred to herein as the degree of acetalization. In the case of polyvinyl formal, the degree of acetalization is also referred to as the degree of formalization.
- Included among the polyvinyl formal resins which may be employed in the present invention are water-insoluble resins having a degree of formalization of not less than 50 mol % and which may be prepared by formalizing polyvinyl alcohols (including partially saponified polyvinyl acetate) or by saponifying and then formalizing polyvinyl acetate. In the present invention, the binder resin is preferably a high hydrophilic polyvinyl formal resin.
- In preparing the adsorbent material, the polyvinyl acetal resin is used in the form of a solution in a water-miscible solvent. By immersing a mixture of the resin and the active carbon adsorbent in an aqueous coagulating solution to effect wet coagulation, the resin binder is permitted adequately to coat the particulate adsorbent or particulate mixture of adsorbent and filler, thus making it possible to add large amounts of filler to the adsorbent material and to provide adsorbent materials having fine microporous structures.
- The choice of the water-miscible solvent for the polyvinyl acetal resin depends upon the type of resin. As the solvent may be used an aqueous solution of inorganic salts, although the inorganic salts themselves have no solvent function.
- When polyvinyl formal resin is used, the solvent is suitably an acid such as formic or acetic acid, a concentrated aqueous solution of formic acid, acetic acid or hydrochloric acid, an aqueous solution of zinc chloride (preferably of concentration 25—35%), an aqueous solution of sodium or potassium thiocyanate (preferably of concentration 30—65%), dimethyl formamide, dimethyl acetamide, dioxane, tetrahydrofuran, dimethylsulphoxide, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol, diethylene glycol or aqueous solutions thereof. For polyvinyl acetal resin, water-miscible lower alcohols such as methanol and ethanol may be used as the solvent in addition to those solvents specified for polyvinyl formal resin. For polyvinyl butyral resin, acetic acid, a concentrated aqueous solution of acetic acid, methanol, ethanol, isopropanol, *n*-propanol, *n*-butanol, acetone, dioxane or ethylene glycol monomethyl ether may be used as the solvent.
- While the solution of polyvinyl acetal resin in the water-miscible solvent may be prepared by merely dissolving said resins in the above solvents, the preparation of a polyvinyl acetal resin solution by acetal formation or saponification followed by acetal formation, for example, of polyvinyl alcohol or polyvinyl acetate dissolved in aqueous solution of acetic acid or zinc chloride is preferred in the commercial practice. The concentration of polyvinyl acetal resin in said solution is varied depending upon the amount of adsorbent to be added, but is generally in the range of from 4 to 20 percent.
- The amount of the adsorbent to be added must be from 0.5 to 20 parts by weight per part by weight of polyvinyl acetal resin so as to give sufficient adsorptive ability to the thus obtained adsorbent materials, it is also necessary in order to retain the strength or mouldability of the adsorbent materials.
- The adsorbents used in the present invention are the various forms of active carbon, e.g. bone-black and activated charcoal, used either alone or in admixture with a non-adsorbent, preferably inorganic, filler, such as a calcium sulphate mineral, including plaster of Paris and gypsum, or with short fibres. These adsorbents are used in particulate form, preferably in the form of powders or granules, and those adsorbents having a wide particles size distribution are particularly preferred.
- In a preferred embodiment of this invention, the adsorbent material is prepared from a polyvinyl acetal resin as binder, having uniformly dispersed therethrough active carbon adsorbent and a non-adsorbent inorganic filler, the adsorbent being present in an amount of from 0.5 to 8 parts by weight per part by weight of resin and the filler being present in an amount of from 0.5 to 10 parts by weight per part by weight of said resin. This material is prepared in the manner described above by mixing the adsorbent and the non-adsorbent filler with a solution of the resin and then bringing the resulting viscous fluid blend into contact with an aqueous coagulating solution, thereby effecting wet coagulation of the resin.
- The efficiency of adsorption can be improved by the combined use of the adsorbent and the non-adsorbent inorganic filler and for this reason it is preferred to use the combination of the two. When an inorganic filler is used, it is preferred that the upper limit on the amount of adsorbent should be 8 parts by weight per part by weight of resin.
- Generally, the particulate adsorbent used alone can produce a satisfactory adsorbent material, however, because the surfaces of the adsorbent particles are coated with a thin film of the polyvinyl acetal resin, the adsorptive capacity of the adsorbent is somewhat reduced and correspondingly the efficiency of adsorption of the resulting adsorbent material is correspondingly decreased. The wet coagulation method alone, when used for solidifying a polyvinyl acetal resin, will produce a resin having a microporous structure, but the degree of microporosity thus achieved is not very high when the wet coagulation is carried out on the resin alone, without the presence of any additional solid matter. However, the addition of a non-adsorbent inorganic

- filler will increase the degree of microporosity in the product obtained in proportion to the amount of the filler added, with the result that the article formed will become highly permeable to liquids, gases and moisture. Thus, the combined use of the particulate adsorbent and the non-adsorbent inorganic particulate filler gives a better adsorptive efficiency than is achieved by the use of the adsorbent alone.
- Although, when using a filler, the adsorbent particles are still coated with a film of the polyvinyl acetal resin, this resin has achieved a greater degree of microporosity as a result of the addition of the particulate inorganic non-adsorbent filler and thus the adsorptive capacity of the adsorbent particles can more easily be fully used.
- The amount of non-adsorbent inorganic particulate filler to be added is suitably chosen depending upon the amount of particulate adsorbent which is to be used with it. The upper and lower limits are determined in the same way as those for the adsorbent. For example, in order for the non-adsorbent filler to be at all effective in enhancing the microporosity of the polyvinyl acetal resin, the lower limit for the amount of filler is 0.5 parts by weight an preferably 1 part by weight per part by weight of polyvinyl acetal resin. The upper limit is usually 10 parts, preferably 8 parts, by weight per part by weight of the resin in order to maintain the strength, mouldability, formability and ease of handling of the resulting adsorbent material.
- Preferably the non-adsorbent fillers used in the invention are of such particle size that they all pass 50 mesh (ASTM) or finer sieves. Examples of suitable inorganic powdery fillers include: calcium sulphate minerals such as plaster of Paris and gypsum, diatomaceous earth, clay, barium sulphate, titanium oxide, aluminium oxide, antimony oxide, calcium silicate, aluminium silicate, calcium carbonate, barium carbonate, pearlite and sericite. Of these, plaster of Paris, gypsum, barium sulphate and titanium oxide are the most desirable.
- The particle size of the adsorbent to be used is suitably chosen depending upon the type of adsorbent material it is desired to prepare, generally the adsorbent selected is a powdery, granular, or partly powdery and partly granular substance having a particle size distribution in the range of 20 to 400 mesh (ASTM).
- In addition to the adsorbent and the filler, if used, the adsorbent materials may contain, where desired, a suitable amount of short fibres, colourants viz. pigments or dyes, modifying resins, softening agent, plasticisers and/or other additives. In particular, short fibres serve to make the resulting formed adsorbent materials softer or more flexible and stronger. Included among the short fibres which are suitable for use are such short inorganic fibres as asbestos fibre and glass fibre. Other fibres which may be used include cellulosic short fibres such as cotton linter and viscose staple fibres (in particular, staple fibres for paper making) and various synthetic fibres such as fibres of polyethylene, polypropylene, polyvinyl chloride, polyamides and polyesters. These short fibres are added to the compositions at the stage where the fluidized mixture is prepared for subsequent forming as by moulding or shaping. Usually, the amount of short fibre added is preferably not more than equivalent to the amount of polyvinyl acetal resin.
- The solution of polyvinyl acetal resin in the water-miscible solvent, e.g. the aqueous solution, which is blended with the adsorbent or mixture of the adsorbent and inorganic filler is preferably a viscous fluidized mixture which is capable of being moulded or otherwise shaped into various forms. Upon treatment in the aqueous coagulating bath, it forms a shaped article having a continuous microporous structure. This is made possible without any special foaming treatment by the nature of the resin itself and by the process of wet coagulation. In order to increase the porosity of the material, the fluidized mixture may be further treated to cause it to produce or contain bubbles. Any of the conventional process may be used for this treatment of the fluidized material, for example, by blowing a gas such as air or carbon dioxide into the fluidized mass or by adding thereto in the presence of an acid a compound which will produce a gas in the presence of an acid, such as calcium carbonate, sodium carbonate, aluminium or zinc, and thereafter subjecting the fluidized material to wet coagulation. Alternatively, the foaming in the fluidized state of the composition into which has been incorporated the foaming agent may be inhibited and the foaming caused to occur in the coagulation bath, thereby further increasing the porosity of the resulting adsorbent material.
- If a polyvinyl acetal resin is dissolved in a water-soluble solvent and the resulting solution is mixed and filled with an inorganic adsorbent or granules of a non-adsorbent powdery filler and the mixture is coagulated by a wet process in an aqueous coagulating bath, the solidified resin exhibits an excellent covering effect upon the inorganic powdery or granular substance, thus firmly gripping the inorganic powder or pulverant material filled therein. Therefore, the adsorbent materials of the present invention may be immersed in water or other liquid or may be vigorously pressed with heavy rubber rollers while the articles are wet or in water, with no danger of the adsorbent filler or inorganic filler being driven out of the products. These articles may be treated with warm or hot water (or even with boiling water) with no adverse after

effect. With these features, the adsorbent materials according to the present invention can be washed and subjected to activation treatments such as deposition and removal of the adsorptive with considerable ease and repeatedly. This is a very important advantage for the adsorbent materials of the invention.

The coagulation of the fluidized mixture is accomplished by bringing it into contact with an aqueous coagulating solution, after the mixture has been shaped or while it is being shaped. In certain cases the mixture may be solidified by exposure to steam. In this case, the steam is condensed to a liquid and consequently, after all, the mixture is solidified in an aqueous coagulating bath. The porous adsorbent materials of the invention usually take the forms of sheets, belts, lengthy sheets in rolls, fibres, various moulded shapes, granules and lumps. In exceptional cases, the fluidized mixture may be solidified by wet coagulation over a substrate such as paper, film, sheet, net, woven or nonwoven cloth, in such a manner that simultaneously with coagulation these substrates are integrated with the adsorbent materials to form complex bodies. As special embodiments of adsorbent materials of the invention, netting, woven or nonwoven cloth, fibres, or slivers may be embedded as backing in such adsorbent materials.

Typical procedures for forming and coagulating adsorbent materials in accordance with the invention are exemplified as follows. Where a sheet-like product is to be obtained, it is desirable to cast the fluidized mixture in a die to form a sheet integrally over a plastic, glass or metal plate or over an endless belt, and then dip it in an aqueous coagulating bath to effect coagulation. In order to obtain a granular or lumpy, particulate, product, for example, the fluidized mixture is generally dropped in the form of granules or lumps into the coagulating bath.

In the present process the aqueous coagulating solution to be used is either water or an aqueous solution of an acid, salt, or water-soluble organic compound, which is heated if necessary. The desirable temperature of the coagulating bath is not lower than 30°C., preferably in the range of 50° to 95°C.

The adsorbent material obtained by the present invention is a porous, preferably microporous, article formed of a polyvinyl acetal resin filled with relatively large amounts of powdery or granular active carbon adsorbent or a mixture of adsorbent and a non-adsorbent inorganic filler in particle form. The apparent specific gravity of the product is largely dictated by the types and amounts of the adsorbent filler and the non-adsorbent filler to be used and by whether a foaming treatment is resorted to or not, but it is usually between about 0.1 and 1.1 at 15°C. The

product is flexible for the relatively large amount of the inorganic substance contained. For example, the product in the form of a long sheet, is sometimes flexible enough to be rolled up with ease. It has been found that the flexibility and softness of the adsorbent articles thus prepared in accordance with the present invention increase in proportion to the increase in the amount of the non-adsorbent inorganic filler in powder form that is added to the composition.

The continuous porous structure of the adsorbent material thus obtained ensures good gas, moisture and liquid permeabilities and also a remarkable liquid adsorbing effect. These features enable the product to have excellent adsorptive capacity for gaseous and liquid phases. Furthermore, the polyvinyl acetal resin employed as the binder imparts a high thermal plasticity to the adsorbent material and permits various hot working of the product, for example, embossing, forming with heat and pressure, and shaping with heat. Thus, the adsorbent materials according to the invention are flexible and are soft, especially when moist, and therefore have many unusual applications. For example, sheet-like products may be wound around pipes in use.

As exemplary modes of use of the adsorbent materials according to the invention, it is possible to make a sheet of adsorbent material and then reduce it on a crusher or pulverizer into granules of adsorbent material. It is further possible to mould the granular adsorbent material with heat and pressure to form articles of various desired shapes, or to sprinkle an adhesive or binder over the mass of adsorbent granules and then mould it and dry the mouldings to obtain variously shaped articles.

The applications for the adsorbent materials of the invention include removal by adsorption of impurities or objectionable substances from gases and liquids and also recovery of various substances by adsorption. More specifically, the adsorbent materials are useful in deodorizing materials in the vapour or liquid phase, removal of impurities by filtration of gases and liquids, and recovery by adsorption of gases and liquids.

The invention is further illustrated by the following Examples, in which, unless otherwise specified, all parts and percentages are by weight and mesh sizes are based on the A.S.T.M. standard sieve.

Example 1

A homogeneous mixture consisting of 10 parts of a completely saponified polyvinyl alcohol (degree of polymerisation 1700), 5.6 parts of formaldehyde, 8 parts of sulphuric acid, 45 parts of acetic acid and 31.4 parts of water. The polyvinyl alcohol was then formalized by heating at 73°C for 5 hours,

whereby a transparent, viscous polyvinyl formal resin solution was obtained. The degree of formalization of the polyvinyl alcohol was 80 mol %.

- 5 The resinous solution was diluted with 70 parts of a 70% aqueous solution of acetic acid and 92 parts of activated charcoal of particle size 30—120 mesh (about 8 times the weight of polyvinyl formal resin) was added
 10 to the solution at a temperature of 40—60°C. The mixture was then kneaded and cooled to a temperature of 20—25°C. After cooling, 0.15 part of metallic aluminium powder of particle size 70 μ was added to the mixture as a blowing agent and the mixture was extruded into sheeting on an endless belt. The resultant sheet was immersed in an aqueous coagulation bath containing 15% acetic acid and about 1.5% sulphuric acid
 20 at a temperature of 65—80°C in order to wet-coagulate the polyvinyl formal resin and simultaneously cause blowing. Since the temperature of the fluid mixture before coagulation was less than 25°C, the reaction of the metallic aluminium and sulphuric acid was inhibited and no substantial blowing occurred by generation of hydrogen gas, however, when the sheet was dipped into the coagulation bath, the temperature was raised and hydrogen generation occurred, with consequent blowing.

The resultant sheeting, after washing with warm water and drying, was about 2 mm in thickness, black in colour, soft, highly flexible and varied from micro-porous to normally porous. It had a specific gravity of 0.30—0.40 at 15°C. The sheeting consisted of approximately 90% activated charcoal and had excellent liquid retention, gas permeability, liquid permeability and adsorptive properties.

This sheeting was compared with granular activated charcoal of grain size 2—3 mm for adsorptive ability and rate of desorption.

The adsorptive ability was compared by measuring the amount of equilibrium adsorption by introducing benzene-saturated air at 50°C, with the following results:

- Adsorptive sheet of Example 1,
 50 46 (g/100 g sample)
 Control (granular activated charcoal),
 48 (g/100 g sample)

The desorption rate was compared for the percentage of desorbed benzene in respect of adsorbed benzene after introducing dry air at 50°C to the sample, which had adsorbed benzene until equilibrium conditions had been reached, for 30 minutes, with the following results:

- 60 Adsorptive sheeting of Example 1 72%
 Control (granular activated charcoal) 51%

The adsorbent materials obtained by the invention show, as shown above, little difference in adsorptive ability from granular activated charcoal, whereas the desorption rate of the former far exceeds that of the latter, and it is clear that the adsorbent materials of the invention have considerable usefulness including much variety in their manner of application.

The activated charcoal in the form of tablets in which resins are used as a binder generally deteriorates in adsorptive ability, while in the invention, notwithstanding that polyvinyl acetal resin is used as a binder, the adsorptive ability of the adsorbent material does not deteriorate, presumably because of the continuous fine porous structure resulting from the coagulation method and the hydrophilic properties of polyvinyl acetal resins.

Example 2

A polyvinyl butyral solution of concentration 8% was prepared by dissolving a polyvinyl butyral resin (degree of butyralization about 67 mol % and average degree of polymerization about 1,000) in aqueous isopropyl alcohol containing 5% water and activated charcoal of grain size 50—150 mesh was added in an amount 8 times the amount of resin. The mixture was then kneaded to form a fluid material which was moulded into the form of a sheet by casting on a glass plate. This was then immersed in an aqueous solution containing 10—20% isopropyl alcohol at 35—45°C to effect wet coagulation. The resultant sheeting was then dried and was found to be 1—3 mm thick with fine pores and had an apparent specific gravity of 0.48 at 15°C. It also exhibited excellent adsorptive properties.

The adsorbent materials in which polyvinyl butyral resin is used are almost equal to materials containing polyvinyl formal resin in adsorptive ability and water permeability but are inferior in thermal properties.

Example 3

An adsorbent sheet having continuous porous structure was obtained in a manner suitable to that of Example 1, except that, in lieu of 92 parts of activated charcoal powder, 60 parts of a mixture of activated charcoal of grain size less than 200 mesh and diatomaceous earth of 50—100 mesh was used. The product had an apparent specific gravity of 0.27.

Example 4

A polyvinyl acetal resin solution was prepared by the method described in Example 1 in which acetaldehyde was used instead of formaldehyde, and, in a manner exactly the same as that of Example 1, adsorbent sheeting consisting mainly of activated charcoal

and polyvinyl acetal resin as a binder was obtained. The resultant sheet had a performance substantially same as when polyvinyl resin was used.

5 **Example 5**

An 8% solution of polyvinyl formal resin in dioxane was produced by dissolving polyvinyl formal resin having a degree of formalization of 84 mol % in aqueous dioxane containing 10% water. 40 Parts of activated charcoal powder having a particle size of 50—200 mesh were then added to 100 parts of said solution and the mixture was then kneaded. This mixture was moulded into sheet and immersed in warm water to effect wet coagulation of the polyvinyl formal, whereby an adsorbent sheeting having fine pores was obtained.

6 **Example 6**

A viscous polyvinyl formal (degree of formalization 79 mol %) solution was produced by the reaction between a mixture of completely saponified polyvinyl alcohol having a polymerization degree of 1,700 formalin (a formalizing agent) and sulphuric acid (catalyst) in a 40% aqueous solution of zinc chloride. The solution was then diluted with a 40% aqueous solution of zinc chloride. Activated charcoal powder having a grain size of 50—150 mesh was added to said solution in an amount of 5 parts by weight per part by weight of the resin. The mixture was kneaded to produce a fluid substance. A small amount of cotton was added to the fluid substance and kneaded at 40—50°C. The mixture was then moulded into sheeting which was further immersed in an aqueous coagulation liquid containing 13% zinc chloride for coagulation. The resultant sheeting had continuous fine pores and an apparent specific gravity of 0.32 at 15°C. It had excellent adsorptive properties, and was soft when wetted with water.

7 **Example 7**

The fluid mixture prepared by adding metallic aluminium to activated charcoal in Example 1 was passed through a perforated metal plate down into warm water for wet-coagulation, and, after washing and drying, an adsorbent material in lumps 3—8 mm dia of apparent specific gravity of about 0.35 at 15°C was obtained.

This material was spread on a metallic plate having a frame and subjected to a thermal compression process between two heated metallic plates at 105—120°C to make an adsorbent material in plate form about 12 mm thick and having an apparent specific gravity of about 0.68 at 15°C.

8 **Example 8**

60 A transparent, viscous polyvinyl formal solution was obtained by the reaction in a homo-

geneous mixture of 10 parts of completely saponified polyvinyl acetate (polymerization degree 1,700), 5.6 parts of formaldehyde, 8 parts of sulphuric acid (catalyst), 45 parts of acetic acid, and 31.4 parts of water at a reaction temperature of 73°C. for 4 hours. By this reaction, 10 parts of saponified polyvinyl acetate converted into 11 parts of polyvinyl formal, and the degree of formalization achieved was about 86 mol %.

65 Next, this resin solution was mixed and diluted with 70 parts of an aqueous solution of acetic acid of concentration 60%. The diluted solution was kept at a temperature of between 50° and 60°C and mixed first with 38.5 parts (or about 3.5 times the amount of polyvinyl formal resin) of dried gypsum dihydrate having a particle size ranging from 10 to 50 microns (powdery non-adsorbent inorganic filler), and was then mixed with 38.5 parts (about 3.5 times the amount of the polyvinyl formal resin) of powdery and granular active carbon having a particle size ranging from 40 to 120 mesh as the powdery and granular adsorbent. Thus a fluidized mixture which could be subsequently shaped to various articles was prepared.

70 (A) The mixture was cast into sheet form over an endless polypropylene belt using a die, and the resultant sheet was dipped in an aqueous coagulating solution containing 20% acetic acid and 1% sulphuric acid at a bath temperature of 80°C. thereby effecting wet coagulation. The coagulation time was 12 minutes. After coagulation, the product in the form of a long sheet was washed with warm water, neutralized with an alkali, washed again, treated with boiling water, and then dried. The sheet so obtained was a fairly strong and flexible long sheet product having a microporous structure, gray in colour and having a thickness of about 1.9 mm and an apparent specific gravity of about 0.63 at 15°C.

75 (B) On the other hand, a fluidized mixture of the same composition as above separately prepared by the same procedure was cooled to 20—30°C., 0.15 part of metallic aluminium powder (having an average particle size of 70 microns) was added as a foaming agent and thoroughly mixed with the mixture, and then, in the same manner as in (A) above, the mixture was shaped into a sheet, solidified (for a coagulation period of about 10 minutes), washed, and dried to a sheet form. The resulting sheet was a long sheet-like article having a thickness of about 2.5 mm and an apparent specific gravity of about 0.55 at 15°C and was grey in color.

80 It comprised a porous structure having considerable strength and flexibility. It could be rolled up. In procedure (B), the metallic aluminium powder (foaming agent) was added to the mixture, but the reaction with sulphuric acid to produce gas was inhibited while the mixture was in

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fluidized state because it was at the comparatively low temperature of between 20° and 30°C. Thus, practically no foaming occurred at this stage. The mixture was spread over a belt in a sheet form and heated in a coagulating bath at 80°C, when, for the first time, gas was produced and foaming took place. The wet coagulation proceeded simultaneously with the foaming. The active carbon content of this sheet product was about 43% by weight.

The adsorptive capacity of the adsorbent material obtained by the produce (B) above was determined. The results are given below:

	Adsorbed gas	Adsorption rate
15	Ammonia gas	27.5%
	Acetic acid gas	29.1%
	Acetaldehyde gas	37.0%

(Note): Adsorption rates are the values determined after adsorption at 50°C for 30 minutes, expressed as a percent by weight of each adsorbed gas on the basis of the total weight of the sheet.

The sheet exhibited outstanding adsorptive capacity for benzene gas, petroleum gas (b.p. 80°—100°C) and chlorine gas, as well as for the gases listed above.

Since this adsorbent material has continuous microporosity porosity, it has not only a good adsorption capacity but also a high adsorption velocity. It has the further merits of high desorption rate and desorption velocity. Furthermore, the product is excellently capable of removing odours (or adsorbing a bad smelling substance) from the atmosphere.

Example 9

Generally in accordance with procedure (B) of Example 8, active carbon (40—120 mesh) was added to a polyvinyl formal resin in an amount of three parts by weight per part by weight of the latter, and, as a non-adsorbent inorganic powdery filler, a mixed powder (gypsum:titanium oxide=70:30 by weight) was added to the polyvinyl formal resin in an amount of 1.5 parts by weight per part by weight of the resin. The mixture was thoroughly mixed to a fluidized mixture, and the mixture was formed and solidified to a sheet-like adsorbent material in the same way as above described.

The product showed adsorbent properties as good as those of the product prepared by procedure (B) of Example 8.

Example 10

(Generally in accordance with procedure (B) of Example 8, active carbon powder (lignite) of from 100 to 300 mesh was added to a polyvinyl formal resin in an amount equivalent to the weight of the resin, and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) having a particle size of 5 to 50 microns was added thereto in an amount of 7 parts per part of the polyvinyl

formal resin. An adsorbent article in the form of a sheet was made in the same way as described in Example 8. The resulting sheet had a thickness of about 2 mm and an apparent specific gravity of about 0.63 at 15°C. The active carbon content of the sheet was as low as 11%, and yet the sheet exhibited good adsorption capacity for acetic acid, acetaldehyde, formaldehyde, ammonia and hydrogen chloride.

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Example 11

A fluidized mixture prepared in accordance with procedure (B) of Example 8 was placed in a round container having a diameter of 15 cm and dipped in water at 70°C. so as to solidify the fluid material. The wet-coagulated matter was washed with warm water and dried, when a dish-like porous adsorbent article having a diameter of about 14.5 cm and a thickness of about 8 mm was obtained.

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Example 12

Using the fluidized material prepared by procedure (B) of Example 8, an adsorbent material was made in the following manner.

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Nonwoven cloth of polyvinyl chloride fibres, about 9 mm in thickness, was dipped in the fluidized mixture and passed through rubber rolls, thereby forcing the fluidized mixture thoroughly into the nonwoven cloth, and finally the impregnated cloth was led through rubber rolls having a certain nip to remove excess mixture from the cloth. The cloth was dipped in an aqueous coagulating bath containing 20% acetic acid and 2% sulphuric acid to effect wet coagulation of the mixture thereon. Next, the cloth was washed with warm water, neutralized with an alkali, rinsed, washed with boiling water, and dried. The product was a porous adsorbent material having a thickness of about 10 mm and an apparent specific gravity of about 0.43. It was strong and considerably flexible. With excellent liquid permeability, the product proved highly useful as an adsorbent-filler for liquids and gases.

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Example 13

A fluidized mixture prepared in accordance with procedure (B) of Example 8 was dropped through holes in a perforated plate into hot water for wet coagulation to small lumps. The lumps were washed and dried, when an adsorbent material in the form of granules and lumps about 2 to 6 mm in diameter and an apparent specific gravity of about 0.50 at 15°C was obtained. This material was placed in a metal die and cast under heat and pressure at 120°C. so that the granules and lumps were put together into an adsorbent plate.

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Example 14

Into a polyvinyl formal resin solution pre-

pared in the same manner as described in Example 8 were incorporated 40 to 200 mesh active carbon in an amount of five times the weight of the polyvinyl formal resin, gypsum powder ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, particle size between 5 and 50 microns) in an amount of four times the weight of the polyvinyl formal resin, and paper-making staple fibres having lengths of 3 mm as fibrous filler in an amount of 0.5 times the weight of the polyvinyl formal resin. With the addition of a suitable amount of a 60% aqueous solution of acetic acid, the mixture was agitated while its viscosity was adjusted to prepare a fluidized mixture to be subsequently shaped. Thereafter, generally in conformity with procedure (B) of Example 8, the mixture was shaped, foamed, and coagulated to form a sheet-like adsorbent article. The sheet was then crushed and ground on a crusher, and the powder thus separated was removed by screening to obtain a granular adsorbent material ranging in particle size from 5 to 20 mesh. Next, the granular adsorbent material was sprayed and sprinkled with a suitable amount of a synthetic rubber latex solution as a binder, charged into a cylindrical metallic container and dried at 70°C. The granules were united altogether in one piece and gave a cylindrical adsorbent article. This article was a highly gas permeable adsorbent material having an apparent specific gravity of about 0.40 at 15°C. It was useful as an adsorbent for use in a cartridge with the metallic container.

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Example 15

A polyvinyl formal resin having a polymerization degree of about 1,200 and a formalization degree of 80 mol % was dissolved in dimethyl formamide to a resin concentration of 8%. To the polyvinyl formal resin solution thus prepared were added an equal amount of active carbon produced from lignite and having a particle size of from 100 to 300 mesh, 4 parts by weight of 100 to 200 mesh activated white clay, 1.5 parts by weight of gypsum powder having a particle size of 5 to 50 microns and 0.5 part by weight of about 200 mesh powdery bentonite, as inorganic fillers (all on the basis of the weight of the polyvinyl formal resin used). The components were thoroughly mixed and suitably diluted to a desired viscosity. The fluidized mixture prepared in this way was shaped, solidified, washed and dried, in the same manner as described in procedure (B) of Example 8, when a sheet-like adsorbent material resulted. This article displayed most desirable properties as an adsorbent-filler for liquids.

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Example 16

A polyvinyl formal resin having a polymerization degree of 1,700 and a formalization degree of about 85 mol % was dissolved

in an aqueous acetic acid solution having a concentration of 60%, to a resin concentration of 10%. To the polyvinyl formal resin solution thus prepared were added 1.5 parts by weight of 80 to 200 mesh active carbon, 1.5 parts of 100 to 200 mesh activated white clay, and an equal amount of fine titanium oxide powder as a non-adsorbent inorganic powdery filler (all on the basis of the weight of the polyvinyl formal resin used). The components were thoroughly mixed to prepare a fluidized mixture to be subsequently shaped.

Next, the mixture was extruded at a constant rate through a hole having a diameter of 1.5 mm. The mixture was extruded into an aqueous coagulation bath and drawn through the bath to produce a string. The product obtained upon washing and drying was a stringy adsorbent material. It was useful as an adsorbent-filler for gases and liquids. When the string was packed into a cylindrical container comprising perforated plates on top and bottom, it exhibited very good liquid permeability and gas permeability and also an excellent adsorption capacity.

Example 17

A sheet-like product, about 2.5 mm thick, which was made by procedure (B) of Example 8, was crushed on a crusher, and the powder was screened off and a granular material having a particle size of about 7 to 12 mesh was collected. The granular material was dipped in an aqueous solution with a concentration of 5% polyvinyl alcohol, carboxy methyl cellulose, or urea formaldehyde resin (initial condensate), or in an emulsion (latex) of a synthetic rubber or synthetic resin having a concentration between 10 and 40%, squeezed lightly and dried so that the granules were sized with one of these resins to retain the minute particles thereof. The material treated in this way was a granular porous adsorbent material, and the product according to the process of the present invention was useful as a granular adsorbent.

WHAT WE CLAIM IS:-

1. An adsorbent material having a continuous porous structure, which comprises a uniform dispersion of particulate active carbon in a polyvinyl acetal resin, the amount of active carbon being from 0.5 to 20 parts by weight per part by weight of said resin.

2. An adsorbent material according to claim 1, in which the amount of said active carbon is from 0.5 to 8 parts by weight per part by weight of said resin.

3. An adsorbent material according to claim 2, additionally comprising from 0.5 to 10 parts by weight of a non-adsorbent filler per part by weight of said resin, said filler being uniformly dispersed through said resin.

4. An adsorbent material according to claim 3, in which said filler is inorganic.

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5. An adsorbent material according to claim 4, in which said filler is gypsum.
6. An adsorbent material according to claim 4, in which said filler is a calcium sulphate mineral, diatomaceous earth, clay, barium sulphate, titanium oxide, aluminium oxide, antimony oxide, calcium silicate, aluminium silicate, calcium carbonate, barium carbonate, pearlite or sericite.
- 10 7. An adsorbent material according to any one of the preceding claim, in which said polyvinyl acetal resin is polyvinyl formal.
8. An adsorbent material according to any one of claims 1 to 6, in which said polyvinyl acetal resin is polyvinyl acetal itself or polyvinyl butyral.
9. An adsorbent material according to any one of the preceding claims, in which said resin has a degree of acetalization of not less than 50 mol %.
- 10 10. An adsorbent material according to any one of the preceding claims, in which said active carbon is activated charcoal or bone-black.
- 25 11. An adsorbent material according to any one of the preceding claims, having a specific gravity of from 0.1 to 1.1 at 15°C.
12. An adsorbent material according to claim 1, substantially as hereinbefore described
- 30 35 with reference to any one of the foregoing Examples.
13. A process for producing an adsorbent material having a continuous porous structure, which comprises mixing a solution of a polyvinyl acetal resin in a water-miscible solvent with from 0.5 to 20 parts by weight per part by weight of said resin of active carbon to produce a homogeneous fluid mixture and coagulating said mixture in an aqueous coagulation bath to produce said material.
14. A process according to claim 13, in which said solution is mixed with from 0.5 to 8 parts by weight per part by weight of said resin of said active carbon.
15. A process according to claim 13, in which said solution is additionally mixed with from 0.5 to 10 parts by weight of a particulate filler, per part by weight of said resin, prior to coagulation of said mixture.
16. A process according to claim 15, in which said particulate filler is gypsum.
17. A process according to any one of claims 13 to 16, in which said polyvinyl acetal resin is a polyvinyl formal.
18. A process according to claim 13, applied to the manufacture of an adsorbent material according to any one of claims 1 to 12.
19. A process according to claim 13, substantially as hereinbefore described.
20. An adsorbent material when prepared by the process of any one of claims 13 to 19.
21. An adsorbent material according to any one of claims 1 to 12 or 20 in the form of a sheet.
22. An adsorbent material according to any one of claims 1 to 12 or 20 in the form of a granule.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.